# Atmospheric Bromine and Ozone Perturbations in the Lower Stratosphere[1]

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ABSTRACT

The role of bromine compounds in the photochemistry of the natural and perturbed stratosphere has been reexamined using an expanded reaction scheme and the results of recent laboratory studies of several key reactions. The most important finding is that through the reaction $BrO + ClO \rightarrow Br + Cl + O_2$ there is a synergistic effect between bromine and chlorine which results in an efficient catalytic destruction of ozone in the lower stratosphere. One-dimensional photochemical model results indicate that BrO is the major bromine species throughout the stratosphere, followed by $BrONO_2$, HBr, HOBr and Br. We show from the foregoing that bromine is more efficient than chlorine as a catalyst for destroying ozone, and discuss the implications for stratospheric ozone of possible future growth in the industrial and agricultural use of bromine. Bromine concentrations of 20 pptv ($2 \times 10^{-11}$), as suggested by recent observations, can decrease the present-day integrated ozone column density by 2.4%, and can enhance ozone depletion from steady-state chlorofluoromethane release at 1973 rates by a factor of 1.1–1.2.

## 1. Introduction

In recent years, photochemical models have been used to understand the factors that control the distribution and column abundance of ozone in the present stratosphere, and to assess the impact of perturbations by stratospheric aviation (Crutzen 1970; Johnston 1971) and the release of chlorofluoromethanes (McElroy *et al.* 1974; Molina and Rowland 1974; Cicerone *et al.* 1974; Wofsy *et al.* 1975a; NAS, 1976; NASA, 1977; Crutzen *et al.* 1978). Although the importance of $HO_x$, $NO_x$ and $Cl_x$ in controlling stratospheric ozone is now well recognized, the close coupling that exists between members of different families has only recently become fully apparent. Indeed, the net effect of these interactions can be subtle, e.g., $ClONO_2$ is a reservoir species for $Cl_x$, but the formation of $ClONO_2$ via the reaction $ClO + NO_2 + M \rightarrow ClONO_2 + M$ can result in either a decrease or in an increase in the catalytic destruction of odd oxygen depending on the photolytic fragmentation products of $ClONO_2$ (Smith *et al.*, 1977; Chang *et al.*, 1979). Although both Watson (1975) and Wofsy *et al.* (1975b) recognized the importance of bromine for catalytic destruction of ozone, neither paper considered the coupling of the chlorine and bromine systems. Derwent and Eggleton (1978) included the coupling of the chlorine and bromine systems in a calculation of ozone depletion in the natural atmosphere due to 10 pptv $Br_x$ and 1.3 ppbv $Cl_x$, but did not discuss the catalytic cycles or the effect on ozone in any detail.

Wofsy *et al.* (1975b) calculated the magnitude of the ozone perturbation by bromine through two catalytic cycles

$$\left.\begin{array}{ll} Br + O_3 \rightarrow BrO + O_2 & (1) \\ BrO + O \rightarrow Br + O_2 & (8) \end{array}\right\} \quad (I)$$

$$\text{Net} \quad O + O_3 \rightarrow 2O_2$$

$$\left.\begin{array}{ll} 2(Br + O_3 \rightarrow BrO + O_2) & (1) \\ BrO + BrO \rightarrow 2Br + O_2 & (9) \end{array}\right\} \quad (II)$$

$$\text{Net} \quad 2O_3 \rightarrow 3O_2$$

However, Wofsy *et al.* (1975b) did not consider the following catalytic cycles:

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$$\left.\begin{array}{lr} Br + O_3 \rightarrow BrO + O_2 & (1) \\ Cl + O_3 \rightarrow ClO + O_2 & (15) \\ BrO + ClO \rightarrow Br + Cl + O_2 & (10a) \end{array}\right\} \quad (III)$$

$$\text{Net} \qquad 2O_3 \rightarrow 3O_2$$

$$\left.\begin{array}{lr} Br + O_3 \rightarrow BrO + O_2 & (1) \\ BrO + NO_2 + M \rightarrow BrONO_2 + M & (11) \\ BrONO_2 + h\nu \rightarrow Br + NO_3 & (J_1) \\ NO_3 + h\nu \rightarrow NO + O_2 & (J_8) \\ NO + O_3 \rightarrow NO_2 + O_2 & (20) \end{array}\right\} \quad (IV)$$

$$\text{Net} \qquad 2O_3 \rightarrow 3O_2$$

$$\left.\begin{array}{lr} Br + O_3 \rightarrow BrO + O_2 & (1) \\ BrO + HO_2 \rightarrow HOBr + O_2 & (12) \\ HOBr + h\nu \rightarrow OH + Br & (J_3) \\ OH + O_3 \rightarrow HO_2 + O_2 & (24) \end{array}\right\} \quad (V)$$

$$\text{Net} \qquad 2O_3 \rightarrow 3O_2$$

$$\left.\begin{array}{lr} Br + O_3 \rightarrow BrO + O_2 & (1) \\ BrO + O_3 \rightarrow Br + 2O_2 & (13) \end{array}\right\} \quad (VI)$$

$$\text{Net} \qquad 2O_3 \rightarrow 3O_2$$

We shall argue that cycle (III) is an example of an interaction between radical species from different families which may provide an important additional photochemical sink for ozone, especially in the lower stratosphere, where competing rate determining reactions such as

$$ClO + O \rightarrow Cl + O_2 \quad (16)$$

$$NO_2 + O \rightarrow NO + O_2 \quad (17)$$

are rapidly falling off with decreasing altitude. Cycle (IV) requires that the photolysis products of $BrONO_2$ and $NO_3$ are $Br + NO_3$ and $NO + O_2$, respectively. For alternative dissociation paths $BrONO_2 \rightarrow BrO + NO_2$, $BrONO_2 \rightarrow O + BrONO$ and $NO_3 \rightarrow NO_2 + O$, the cycle would not result in a net destruction of ozone. This paper will discuss the close coupling of the $Br_x$ system with the $HO_x$, $NO_x$ and $Cl_x$ systems with emphasis on the reactions

$$BrO + h\nu \rightarrow Br + O \quad (J_2)$$

$$BrO + ClO \rightarrow Br + Cl + O_2 \quad (10a)$$

$$BrO + NO_2 + M \rightarrow BrONO_2 + M \quad (11)$$

$$BrO + HO_2 \rightarrow HOBr + O_2 \quad (12)$$

which have not been previously examined. Our discussion also includes other catalytic cycles involving $Cl_x$-$NO_x$ and $Cl_x$-$HO_x$ systems which might also lead to an efficient destruction of ozone in the lower stratosphere:

$$\left.\begin{array}{lr} Cl + O_3 \rightarrow ClO + O_2 & (15) \\ ClO + NO_2 + M \rightarrow ClONO_2 + M & (19) \\ ClONO_2 + h\nu \rightarrow Cl + NO_3 & (J_{10}) \\ NO_3 + h\nu \rightarrow NO + O_2 & (J_8) \\ NO + O_3 \rightarrow NO_2 + O_2 & (20) \end{array}\right\} \quad (VII)$$

$$\text{Net} \qquad 2O_3 \rightarrow 3O_2$$

$$\left.\begin{array}{lr} Cl + O_3 \rightarrow ClO + O_2 & (15) \\ ClO + HO_2 \rightarrow HOCl + O_2 & (21) \\ HOCl + h\nu \rightarrow OH + Cl & (J_9) \\ OH + O_3 \rightarrow HO_2 + O_2 & (24) \end{array}\right\} \quad (VIII)$$

$$\text{Net} \qquad 2O_3 \rightarrow 3O_2$$

We may note that in all one-dimensional modeling studies of the effect of halogenated compounds on $O_3$ (see, e.g., Chang 1976; Logan *et al.* 1978), perturbations above 25 km are significantly larger than those between 16 and 25 km. The present work raises the possibility of additional $O_3$ reductions in the lower stratosphere not considered in the previous works. In another paper (Wang *et al.* 1979), we calculate the effects of $O_3$ depletion in the lower stratosphere on the earth's surface temperature. A net cooling of the surface ($\Delta T_s \approx -0.3$ K) could result, a value which is sufficient to nearly cancel the chlorofluoromethane-induced greenhouse effect.

## 2. Photochemistry of bromine compounds

Table 1a summarizes the reactions involving bromine-containing species, thought to be important in the photochemistry of the stratosphere, along with the preferred values of their rate coefficients. As will be shown later, the partitioning of inorganic bromine into its constituent species ($Br_x \equiv HBr + BrONO_2 + BrO + HOBr + Br$), and the magnitude of its effect on ozone, is sensitive to only a few of these rate coefficients. The reaction scheme is similar to that suggested by Watson (1975) and Wofsy *et al.* (1975b), but has been expanded somewhat to include the formation and destruction of $BrONO_2$, and HOBr and the interaction between the $Br_x$ and $Cl_x$ systems. The basic set of key reactions in the $Br_x$ system is similar to that in the $Cl_x$ system, with a few important exceptions: 1) hydrogen atom abstraction by atomic bromine from $H_2$ and $CH_4$ are highly endothermic; consequently, these reactions are too slow to be important in the stratosphere; and 2) radical-radical processes such as the bimolecular disproportionation of BrO radicals may play an important role in $Br_x$ chemistry (the magnitude of the effect is critically dependent on the mixing ratio of total inorganic bromine), whereas their chlorine analogs are thought to be of little importance; and 3) the photolysis rate for BrO is two to three orders of magnitudes faster than that for ClO.

Atomic bromine can be converted into the inactive form of HBr by three processes:

$$Br + HO_2 \rightarrow HBr + O_2 \quad (2)$$

$$Br + H_2O_2 \rightarrow HBr + HO_2 \quad (3)$$

$$Br + H_2CO \rightarrow HBr + HCO \quad (4)$$

An estimated value of $2 \times 10^{-11}$ cm$^3$ s$^{-1}$ has been used for $k_2$ in most of our calculations as there has not been a direct study of this reaction using a modern kinetic technique. The sensitivity of our model to the absolute value of $k_2$ has been tested by using values of 0.5 and $4 \times 10^{-11}$ cm$^3$ s$^{-1}$. Using the upper limit tabulated for $k_3$, it can be shown that reaction (3) is not an important loss mechanism for Br. It can also be shown that reaction (4) is unlikely to be comparable in magnitude to reaction (2) as a loss process for Br, as $k_4$ would have to be greater than $1 \times 10^{-12}$ cm$^3$ s$^{-1}$ at stratospheric temperatures (this assumes that the mixing ratio for $H_2CO$ is ~0.1 ppbv), whereas an estimated value of $\leqslant 10^{-13}$ cm$^3$ s$^{-1}$ is more realistic. Consequently, the only important formation process for HBr is reaction (2) (the formation of HBr via the reaction of BrO with OH is discussed later). The major process by which atomic bromine is regenerated from HBr is

$$OH + HBr \rightarrow H_2O + Br \quad (5)$$

Other minor loss mechanisms for HBr are

$$HBr + h\nu \rightarrow J + Br \quad (J_5)$$

$$HBr + O \rightarrow OH + Br \quad (6)$$

Since the calculations of Wofsy *et al.* (1975b), the rate coefficients for

$$HO_2 + NO \rightarrow OH + NO_2 \quad (22)$$

$$HO_2 + O_3 \rightarrow OH + 2O_2 \quad (18)$$

have been revised (Howard and Evenson 1977; Howard 1978), resulting in higher concentrations of OH, and lower concentrations of $HO_2$ and $H_2O_2$. The net result is that the Br:HBr ratio is significantly higher in the present model than in previous models. We may note that the Br:HBr ratio is significantly higher than the Cl:HCl ratio in the stratosphere due to slower rates of formation of HBr compared to HCl, combined with the much greater reactivity of HBr, over HCl, toward OH radicals.

The other major pathway for atomic bromine is its reaction with $O_3$ to form BrO:

$$Br + O_3 \rightarrow BrO + O_2 \quad (1)$$

Once formed, BrO participates in a series of reactions similar to those of the ClO radical in the $Cl_x$ system:

$$BrO + h\nu \rightarrow Br + O \quad (J_2)$$

$$BrO + NO \rightarrow Br + NO_2 \quad (7)$$

$$BrO + O \rightarrow Br + O_2 \quad (8)$$

$$BrO + BrO \rightarrow 2Br + O_2 \quad (9a)$$

$$\rightarrow Br_2 + O_2 \quad (9b)$$

$$BrO + ClO \rightarrow Br + Cl + O_2 \quad (10a)$$

$$\rightarrow Br + OClO \quad (10b)$$

$$BrO + NO_2 + M \rightarrow BrONO_2 + M \quad (11)$$

$$BrO + HO_2 \rightarrow HOBr + O_2 \quad (12)$$

$$BrO + O_3 \rightarrow Br + 2O_2 \quad (13)$$

$$BrO + OH \rightarrow HO_2 + Br \quad (14a)$$

$$\rightarrow HBr + O_2 \quad (14b)$$

Reactions ($J_2$), (7), (8) and (11)–(14) play the same roles as their chlorine analogs. Using the absorption data obtained by Durie and Ramsay (1958) and Clyne and Cruse (1970), we repeat Watson's (1975) analysis and estimate a diurnally averaged photolysis rate $J_2 = 1 \times 10^{-2}$ s$^{-1}$ (including corrections for Rayleigh scattering and ground albedo). Since the possibility of continuum absorption underlying the series of bands in the region 289–355 nm is not ruled out from either Durie and Ramsay's (1958) or Clyne and Cruse's (1970) data, $J_2$ could be as high as $3 \times 10^{-2}$ s$^{-1}$. In the stratosphere, reactions ($J_2$) and (7) are both important, but not as effective in limiting the catalytic efficiency of $Br_x$ as the NO + ClO reaction is in the $Cl_x$ system. The primary reason is that while BrO is the major form of $Br_x$, ClO is not the major form of $Cl_x$ in the stratosphere. Although the rate coefficient for reaction (8) is uncertain by a factor of 3 this does not introduce a significant uncertainty in the magnitude of the ozone perturbation, for reasons which will be discussed in the section on atmospheric modeling. The formation and destruction of $BrONO_2$ through

$$BrO + NO_2 + M \rightarrow BrONO_2 + M \quad (11)$$

$$BrONO_2 + h\nu \rightarrow Br + NO_3 \quad (J_1)$$

results in cycle (IV). The rate coefficient for reaction (11) is taken to be twice that for the formation of $ClONO_2$ via reaction (19), based on data collected between 50 and 700 Torr at 298 K by Sander *et al.* (1979)

Reactions (9a) and (9b) [BrO + BrO] are several orders of magnitude faster than reactions (23a), (23b) and (23c) [ClO + ClO]. Therefore, reactions (9a) and (9b) can become important at high BrO concentrations ($Br_x \geqslant 100$ pptv). Even though the branching ratio of reaction (9) has been incorporated into the model, it is unimportant as $Br_2$ undergoes

TABLE 1a. Partial list of essential reactions discussed in this paper with their preferred rate coefficients. We use the rate coefficients recommended by NASA (1977), except as otherwise given in this table. The units for diurnally averaged photolysis rates ($J$), two-body and three-body reactions ($k$) are $s^{-1}$, $cm^3\ s^{-1}$ and $cm^6\ s^{-1}$, respectively. The numerical values or $J$ refer to 40, 30 and 20 km for 30°N, spring–fall season.

| | | |
|---|---|---|
| $BrONO_2 + h\nu \rightarrow Br + NO_3$ | $J_1 = 1.6 \times 10^{-3}, 1.1 \times 10^{-3}, 9.8 \times 10^{-4}$ | (d) |
| $BrO + h\nu \rightarrow Br + O$ | $J_2 = 1 \times 10^{-2}$ | (e) |
| $HOBr + h\nu \rightarrow OH + Br$ | $J_3 = 1.7 \times 10^{-3}, 1.3 \times 10^{-3}, 1.1 \times 10^{-3}$ | (f) |
| $Br_2 + h\nu \rightarrow Br + Br$ | $J_4 = 1.5 \times 10^{-2}$ | (g) |
| $HBr + h\nu \rightarrow H + Br$ | $J_5 = 5.8 \times 10^{-6}, 4.9 \times 10^{-6}, 2.8 \times 10^{-9}$ | (c) |
| $CH_3Br + h\nu \rightarrow CH_3 + Br$ | $J_6 = 7.3 \times 10^{-6}, 4.1 \times 10^{-8}, 2.2 \times 10^{-9}$ | (c) |
| $NO_3 + h\nu \rightarrow NO_2 + O$ | $J_7 = 1 \times 10^{-2}$ | (a) |
| $NO_3 + h\nu \rightarrow NO + O_2$ | $J_8 = 5 \times 10^{-3}$ | (a) |
| $HOCl + h\nu \rightarrow OH + Cl$ | $J_9 = 2 \times 10^{-4}$ | (h) |
| $ClONO_2 + h\nu \rightarrow Cl + NO_3$ | $J_{10} = 3.5 \times 10^{-4}, 8.8 \times 10^{-5}, 5.7 \times 10^{-5}$ | (a) |
| $NO_2 + h\nu \rightarrow NO + O$ | $J_{11} = 7.5 \times 10^{-3}$ | (a) |
| $HNO_3 + h\nu \rightarrow OH + NO_2$ | $J_{12} = 2.8 \times 10^{-5}, 5.7 \times 10^{-6}, 3.9 \times 10^{-7}$ | (a) |
| $Br + O_3 \rightarrow BrO + O_2$ | $k_1 = 1.4 \times 10^{-11}e^{-755/T}$ | (i) |
| $Br + HO_2 \rightarrow HBr + O_2$ | $k_2 = 2 \times 10^{-11}$ | (j) |
| $Br + H_2O_2 \rightarrow HBr + HO_2$ | $k_3 < 2 \times 10^{-12}e^{-1400/T}$ | (k) |
| $Br + H_2CO \rightarrow HBr + HCO$ | $k_4 \leqslant 1 \times 10^{-13}$ | (l) |
| $OH + HBr \rightarrow H_2O + Br$ | $k_5 = 8.5 \times 10^{-12}$ | (m) |
| $O + HBr \rightarrow OH + Br$ | $k_6 = 7.6 \times 10^{-12}e^{-1571/T}$ | (n) |
| $BrO + NO \rightarrow Br + NO_2$ | $k_7 = 8.7 \times 10^{-12}e^{265/T}$ | (o) |
| $BrO + O \rightarrow Br + O_2$ | $k_8 = 3 \times 10^{-11}$ | (p) |
| $BrO + BrO \rightarrow 2Br + O_2$ | $k_{9a} = 2.1 \times 10^{-12}e^{244/T}$ | (q) |
| $\rightarrow Br_2 + O_2$ | $k_{9b} = 3.5 \times 10^{-13}e^{244/T}$ | |
| $BrO + ClO \rightarrow Br + Cl + O_2$ | $k_{10a} = 6.7 \times 10^{-12}$ | (r) |
| $\rightarrow Br + OClO$ | $k_{10b} = 6.7 \times 10^{-12}$ | |
| $BrO + NO_2 + M \rightarrow BrONO_2 + M$ | $k_{11} = 2k_{19}$ | (s) |
| $BrO + HO_2 \rightarrow HOBr + O_2$ | $k_{12} = 4 \times 10^{-12}$ | (t) |
| $BrO + O_3 \rightarrow Br + 2O_2$ | $k_{13} < 1 \times 10^{-12}e^{-1600/T}$ | (u) |
| $BrO + OH \rightarrow HO_2 + Br$ | $k_{14a}$ | (v) |
| $\rightarrow HBr + O_2$ | $k_{14b}$ | |
| $Cl + O_3 \rightarrow ClO + O_2$ | $k_{15}$ | (a) |
| $ClO + O \rightarrow Cl + O_2$ | $k_{16}$ | (a) |
| $NO_2 + O \rightarrow NO + O_2$ | $k_{17}$ | (a) |
| $HO_2 + O_3 \rightarrow OH + 2O_2$ | $k_{18} = 1.1 \times 10^{-14}e^{-580/T}$ | (b) |
| $ClO + NO_2 + M \rightarrow ClONO_2 + M$ | $k_{19}$ | (a) |
| $NO + O_3 \rightarrow NO_2 + O_2$ | $k_{20}$ | (a) |
| $ClO + HO_2 \rightarrow HOCl + O_2$ | $k_{21} = 3.8 \times 10^{-12}$ | (b) |
| $HO_2 + NO \rightarrow NO_2 + OH$ | $k_{22} = 3.4 \times 10^{-12}e^{250/T}$ | (b) |
| $ClO + ClO \rightarrow$ products | $k_{23}$ | (a) |
| $OH + O_3 \rightarrow HO_2 + O_2$ | $k_{24}$ | (a) |
| $Cl + CH_4 \rightarrow HCl + CH_3$ | $k_{25} = 9.9 \times 10^{-12}e^{-1359/T}$ | (b) |
| $OH + C_2H_4Br_2 \rightarrow$ products | $k_{26} = 2.5 \times 10^{-13}$ | (w) |
| $OH + CF_3Br \rightarrow$ products | $k_{27} < 1 \times 10^{-15}$ | (x) |
| $OH + CHBr_3 \rightarrow$ products | $k_{28} = 4.7 \times 10^{-12}e^{-1134/T}$ | (y) |
| $OH + CH_3CBr_3 \rightarrow$ products | $k_{29} = 2.5 \times 10^{-12}e^{-1450/T}$ | (y) |
| $OH + CH_3Br \rightarrow CH_2Br + H_2O$ | $k_{30} = 7.9 \times 10^{-13}e^{-889/T}$ | (y) |
| $ClO + NO \rightarrow Cl + NO_2$ | $k_{31}$ | (a) |
| $HCl + OH \rightarrow H_2O + Cl$ | $k_{32}$ | (a) |
| $Cl + H_2CO \rightarrow HCl + HCO$ | $k_{33} = 7.5 \times 10^{-11}$ | (z) |

(a) NASA (1977).
(b) NASA (1979).
(c) Wofsy *et al.* (1975a,b).
(d) Spencer and Rowland (1978), recommended by b.
(e) Based on Durie and Ramsay (1958) and Clyne and Cruse (1970).
(f) Based on Molina and Molina (private communication, 1979) cross section for HOCl, red-shifted by 300 nm.
(g) Calvert and Pitts (1966).
(h) Molina and Molina (1979).
(i) Evaluated from the data of Clyne and Watson (1975), Leu and DeMore (1977), Michael *et al.* (1979) and Michael and Payne (1979), recommended by b.
(j) Estimated.
(k) Based upon the unpublished upper limit reported for $k$(298K) by Leu and DeMore, recommended by b.
(l) Estimated.
(m) Mean of values reported by Takacs and Glass (1973a) and Ravishankara *et al.* (private communication, 1979), recommended by b.
(n) NASA 1010, based upon Tackacs and Glass (1973b), Brown and Smith (1975) and Singleton and Cvetanovic (1976, based on paper presented at the 12th Informal Conference on Photochemistry, NBS, Washington, DC).

TABLE 1a. (*Continued*)

(o) Watson *et al.* (1979).
(p) NASA (1977), based upon Clyne *et al.* (1976).
(q) Sander and Watson (1979).
(r) NASA (1977), Clyne and Watson (1977).
(s) Based on provisional data obtained between 50 and 700 Torr $N_2$ at 298 K, by Sander *et al.* (1979).
(t) Estimate based on $k(ClO + HO_2)$.
(u) Estimated Arrhenius expression based upon upper limit of $5 \times 10^{-15}$ $cm^3$ $s^{-1}$ at 298 K reported by Sander and Watson (1979), not included in normal model (see text).
(v) See text.
(w) Howard *et al.* (1975).
(x) LeBras and Combourieu (1978).
(y) Based on chlorine analogs (Davis *et al.*, 1976; Watson *et al.*, 1977).
(z) Stief *et al.* (1978).

rapid photolysis in the stratosphere. $Cl_x$ and $Br_x$ reactions are unimportant at night as both ClO and BrO are tied up as $ClONO_2$ and $BrONO_2$, respectively. The $Cl_x$ and $Br_x$ systems are coupled through reactions (10a) and (10b). It is unimportant whether process (10a) actually proceeds through either Br + ClOO or Cl + BrOO as both peroxy radicals undergo rapid thermal decomposition. Even if the products were BrCl + $O_2$, it is equivalent to writing Br + Cl + $O_2$ as BrCl rapidly photolyzes in the stratosphere. Unfortunately reaction (10a), which is the key reaction, has only been studied at 298 K and the two published studies report values which differ by a factor of 3; $k_{10a}$ could exhibit either a small positive or negative temperature dependence. Reaction (10b) only participates in a net-nothing cycle, as the photolysis products of OClO are $O(^3P)$ and ClO:

$$\begin{array}{lr} Br + O_3 \rightarrow BrO + O_2 & (1) \\ BrO + ClO \rightarrow Br + OClO & (10b) \\ OClO + h\nu \rightarrow O + ClO & \\ O + O_2 + M \rightarrow O_3 + M & \\ \hline \text{Net} \quad \text{nothing} & \end{array}$$

For cycles (V) and (VI) to be important, the rate-limiting steps (12) and (13) must be comparable to the rate-limiting steps in cycles (I)–(IV). The important formation and destruction processes for HOBr are

$$HO_2 + BrO \rightarrow HOBr + O_2 \quad (12)$$

$$HOBr + h\nu \rightarrow OH + Br \quad (J_3)$$

The steady-state concentration of HOBr is

$$[HOBr] = k_{12}[HO_2][BrO]/J_3.$$

Substituting our best estimates for $k_{12}$ and $J_3$ (see Table 1a) results in a ratio of ~0.1 for [HOBr]/[BrO]. Therefore, HOBr is not a significant reservoir of $Br_x$. In the current atmosphere (assuming 20 pptv $Br_x$ and 2.3 ppbv $Cl_x$) cycle (V) is not important unless $k_{12} \gg 4 \times 10^{-12}$ $cm^3$ $s^{-1}$, an unlikely possibility. Cycle (VI) does not become important unless $k_{13} \gg 3 \times 10^{-16}$ $cm^3$ $s^{-1}$ at stratospheric temperatures. An upper limit of $\leqslant 5 \times 10^{-15}$ $cm^3$ $s^{-1}$ has recently been reported for $k_{13}$ at 298 K by Sander and Watson (1979). However, it must be stressed that no reaction was observed, and that the chlorine analog of reaction (13) is very slow with an upper limit of ~$10^{-18}$ $cm^3$ $s^{-1}$ (Lin *et al.* 1975). In our calculations we do not include reaction (13).

The OH + BrO reaction (14) has not been included in the model as neither the overall rate coefficient nor the product distribution is known. Although reaction (14a) can participate in the catalytic cycle

$$\begin{array}{lr} Br + O_3 \rightarrow BrO + O_2 & (1) \\ OH + BrO \rightarrow Br + HO_2 & (14a) \\ HO_2 + O_3 \rightarrow OH + 2O_2 & (18) \\ \hline \text{Net} \quad 2O_3 \rightarrow 3O_2 & \end{array}$$

it is unimportant as the magnitude of the rate-determining step is not comparable to those in cycles (I)–(IV) unless $k_{14a} \gg 10^{-10}$ $cm^3$ $s^{-1}$ which is quite unlikely (the magnitude of $k_{14}$ is expected to be quite similar to $k(OH + ClO)$ which has recently been reported to be $9.1 \times 10^{-12}$ $cm^3$ $s^{-1}$ at 298 K by Leu and Lin (1979). Reaction (14b) can be important in reducing the catalytic efficiency of $Br_x$ by decreasing the $BrO/Br_x$ ratio. For reaction (14b) to be important the magnitude of $k_{14b}[OH][BrO]$ must be comparable to $k_2[Br][HO_2]$ in order to influence the rate of formation of HBr and the partitioning of $Br_x$. This occurs when $k_{14b}/k_2 \approx 0.1$, i.e., $k_{14b} \approx 2 \times 10^{-12}$ $cm^3$ $s^{-1}$.

### 3. Atmospheric modeling

Singh *et al.*'s (1977) measurements of halogenated organic species indicate that methyl bromide ($CH_3Br$) is probably the major bromine species in the troposphere with concentrations ranging from 1 to 300 pptv. The average concentration is ~5–10 pptv in clean air and 20 pptv in marine air (Singh, 1979, private communication). The main source of $CH_3Br$ is marine biological activity (Lovelock, 1975). There

TABLE 1b. List of reactions used in our model in addition to those given in Table 1a. Values for the mean dissociation rate $J$ are given for 40 km.

| Reaction | $J$ |
|---|---|
| $O_2 + h\nu \rightarrow 2O$ | 1.8 (−10) |
| $O_3 + h\nu \rightarrow O_2 + O$ | 9.0 (−4) |
| $O_3 + h\nu \rightarrow O_2 + O(^1D)$ | 6.8 (−4) |
| $H_2O + h\nu \rightarrow H + OH$ | 6.6 (−10) |
| $H_2O_2 + h\nu \rightarrow 2OH$ | 1.9 (−5) |
| $N_2O + h\nu \rightarrow N_2 + O(^1D)$ | 1.4 (−7) |
| $NO + h\nu \rightarrow N + O$ | 9.1 (−8) |
| $N_2O_5 + h\nu \rightarrow NO_2 + NO_3$ | 9.8 (−5) |
| $Cl_2 + h\nu \rightarrow 2Cl$ | 1.2 (−3) |
| $HCl + h\nu \rightarrow H + Cl$ | 8.6 (−8) |
| $ClO + h\nu \rightarrow Cl + O$ | 6.2 (−5) |
| $CFCl_3 + h\nu \rightarrow$ products | 3.4 (−6) |
| $CF_2Cl_2 + h\nu \rightarrow$ products | 3.8 (−7) |
| $CH_3Cl + h\nu \rightarrow$ products | 7.7 (−8) |
| $CCl_4 + h\nu \rightarrow$ products | 1.6 (−5) |
| $COF_2 + h\nu \rightarrow$ products | 9.5 (−8) |
| $COFCl + h\nu \rightarrow$ products | 1.3 (−6) |
| $CO_2 + h\nu \rightarrow CO + O$ | 1.8 (−11) |
| $CH_4 + h\nu \rightarrow CH_3 + H$ | 6.4 (−36) |
| $CH_2O + h\nu \rightarrow CHO + H$ | 1.5 (−5) |
| $CH_2O + h\nu \rightarrow H_2 + CO$ | 2.4 (−5) |
| $CH_3OOH + h\nu \rightarrow CH_3O + OH$ | 1.9 (−5) |
| **Reaction** | **$k$** |
| $O^1D + O_2 \rightarrow O + O_2$ | (a) |
| $O^1D + N_2 \rightarrow O + N_2$ | (a) |
| $O^1D + H_2O \rightarrow OH + OH$ | (a) |
| $O^1D + H_2 \rightarrow H + OH$ | (a) |
| $O^1D + CH_4 \rightarrow CH_3 + OH$ | (a) |
| $O^1D + N_2O \rightarrow NO + NO$ | (a) |
| $O^1D + N_2O \rightarrow N_2 + O_2$ | (a) |
| $O + O_2 + M \rightarrow O_3 + M$ | (b) |
| $O_3 + O \rightarrow 2O_2$ | (b) |
| $O + O + M \rightarrow O_2 + M$ | (b) |
| $N + O_3 \rightarrow NO + O_2$ | (b) |
| $O + OH \rightarrow O_2 + H$ | (a) |
| $O + HO_2 \rightarrow OH + O_2$ | (a) |
| $H + O_3 \rightarrow OH + O_2$ | (a) |
| $H + O_2 + M \rightarrow HO_2 + M$ | (a) |
| $N + O_2 \rightarrow NO + O$ | (a) |
| $N + NO \rightarrow N_2 + O$ | (a) |
| $OH + NO^2 + M \rightarrow HNO_3 + M$ | (a) |
| $OH + HNO_3 \rightarrow H_2O + NO_3$ | (a) |
| $OH + HO_2 \rightarrow H_2O + O_2$ | (a) |
| $H + HO_2 \rightarrow H_2 + O_2$ | (b) |
| $H + HO_2 \rightarrow OH + OH$ | (b) |
| $H + HO_2 \rightarrow H_2O + O$ | (b) |
| $HO_2 + HO_2 \rightarrow H_2O_2 + O_2$ | (a) |
| $H_2O_2 + OH \rightarrow H_2O + HO_2$ | (a) |
| $H_2O_2 + O \rightarrow OH + HO_2$ | (a) |
| $OH + CH_4 \rightarrow CH_3 + H_2O$ | (a) |
| $NO_3 + NO \rightarrow NO_2 + NO_2$ | (b) |
| $NO_2 + O_3 \rightarrow NO_3 + O_2$ | (a) |
| $NO_3 + NO_2 + M \rightarrow N_2O_5 + M$ | (b) |
| $NO_2 + NO_3 \rightarrow NO_2 + O_2 + NO$ | (b) |
| $Cl + HO_2 \rightarrow HCl + O_2$ | $4.1 \times 10^{-11}$ (d) |
| $CO + OH \rightarrow CO_2 + H$ | (a) |
| $H_2 + OH \rightarrow H_2O + H$ | (b) |
| $HNO_3 + O \rightarrow OH + NO_3$ | (b) |
| $N_2O_5 + M \rightarrow NO_2 + NO_3 + M$ | (b) |
| $Cl + Cl + M \rightarrow Cl_2 + M$ | (b) |
| $ClNO_3 + O \rightarrow ClO + NO_3$ | (a) |
| $Cl + H_2 \rightarrow HCl + H$ | (a) |
| $Cl + O_2 + M \rightarrow ClOO + M$ | (a) |
| $CH_3Cl + OH \rightarrow$ products | (a) |
| $ClOO + M \rightarrow Cl + O_2 + M$ | (b) |
| $CH_3O_2 + NO \rightarrow CH_3O + NO_2$ | (b) |
| $CH_3O + O_2 \rightarrow CH_2O + HO_2$ | (a) |
| $CH_3O_2 + CH_3O_2 \rightarrow 2\,CH_3O + O_2$ | (b) |
| $CH_2O + OH \rightarrow CHO + H_2O$ | (b) |
| $CHO + O_2 \rightarrow O + HO_2$ | (a) |
| $CH_3O_2 + HO_2 \rightarrow CH_3OOH + O_2$ | (b) |
| $CH_3OOH + OH \rightarrow CH_3O_2 + H_2O$ | (c) |
| $CH_3 + O_2 + M \rightarrow CH_3O_2 + M$ | (c) |
| $CH_3 + O_2 \rightarrow CH_2O + OH$ | (c) |

(a) NASA (1977).
(b) Logan *et al.* (1978).
(c) Wofsy (1976).
(d) DeMore (1978, private communication). This value is close to $4.5 \times 10^{-11}$ recommended by NASA (1979).

is a smaller contribution from anthropogenic sources, associated with its use as a soil fumigant. Other bromine compounds such as dibromomethane ($CH_2Br_2$), bromoform ($CHBr_3$) and dibromochloromethane ($CHClBr_2$) could also be produced in the marine environment and subsequently released to the atmosphere (Burreson *et al.*, 1975; Theiler *et al.*, 1978; Helz and Hsu 1978), but they have not yet been detected in the atmosphere. Leinster *et al.* (1978) and Singh (1979, private communication) have detected ethylene dibromide in urban air. Its concentration lies in the range from 0.1 to 20 pptv, and is clearly related to the use of ethylene dibromide as a gasoline additive. Spencer and Rowland (1978) have suggested that additional anthropogenic sources of bromine could come from some bromofluorocarbon compounds (e.g., $CF_3Br$, $CF_2BrCF_2Br$) which are used extensively as flame retardants, and will be ultimately released to the atmosphere. The lifetimes and source strengths of important organic bromine species are summarized in Table 2. Compounds with long lifetimes in the troposphere are eventually transported into the stratosphere, where they can be readily decomposed to provide a source of inorganic stratospheric bromine.

In the stratosphere the presence of small concentrations of bromine was first reported by Lazrus *et al.* (1976), using an air filter technique for capturing stratospheric halogens from a balloon platform. Recently, Lazrus *et al.* (1979) performed a comprehensive set of measurements of stratospheric bromine and chlorine, using analytical techniques that include neutron activation analysis. Neither the neutral nor base-impregnated filters collect organic compounds (e.g., $CH_3Br$, $CF_3Br$). The collection efficiencies for the alkaline-based filters have been calibrated for HCl, ClO, $ClONO_2$, HBr and BrO, but not for $BrONO_2$ or HOBr. However, we do not expect large deviations in collection

TABLE 2. Lifetimes and sources of important organic bromine compounds.

| | $CH_3Br$ | $C_2H_4Br_2$ | $CF_3Br$ | $CHBr_3$ | $CH_3CBr_3$ |
|---|---|---|---|---|---|
| Globally averaged mixing ratio (pptv) | 5–10 (a) | 0.1–1 (b) | <1 (c) | (d) | (d) |
| Major sink | $CH_3Br + OH$(e) | $C_2H_4Br_2 + OH$(e) | $CF_3Br + h\nu$(f) | $CHBr_3 + OH$(e) | $CH_3CBr_3 + OH$(c) |
| Mean lifetime | 2.1 years | 3 months | 70 years | 1 year | 5.7 years |
| Globally averaged source strength ($10^9$ gm Br year$^{-1}$) | 35–70 | 12–120 | <0.21 | (d) | (d) |
| Global industrial production ($10^9$ gm Br year$^{-1}$) (g) | 14 (h) | 182 (h) | 1.1 (h, i) | (d) | (d) |

(a) Based on Singh *et al.* (1977), and Singh (1979, private communication).
(b) Estimated from Leinster *et al.* (1979). These numbers must be considered as illustrative rather than representative of true mean values.
(c) Singh (1979, private communication).
(d) Information not available.
(e) We assume a mean tropospheric OH concentration of $5 \times 10^5$ cm$^{-3}$ (Singh, 1977; Chang and Penner, 1978). The rate coefficients are given in Table 1.
(f) Based on dissociation cross-sections measured by Molina and Molina (1979)
(g) A much more difficult quantity to estimate is the release rate to the atmosphere, which probably ranges from 10 to 50% of the production rate for most of the compounds considered here.
(h) Based on 1975 and 1976 data published in Bureau of Mines Yearbook, U.S. Department of Interior. Since the United States accounts for 67% of all bromine produced, we estimate the global production rate by multiplying the U.S. production rate by a factor of 1.5.
(i) Based on U.S. 1976 production of $0.75 \times 10^9$ gm Br, see text.

efficiencies among the major inorganic halogen species. Fig. 1 shows the mixing ratio for total inorganic bromine $Br_x(=Br + 2Br_2 + BrO + HBr + BrONO_2 + HOBr)$ at 19 km, from the equator to 70°N. The dots and crosses represent data obtained in April 1976 and July 1977, respectively. The noticeable increase in $Br_x$ both as a function of altitude and latitude suggests that stratospheric bromine is derived from a tropospheric precursor, such as $CH_3Br$ or $CF_3Br$. In subsequent computations, we shall assume that all $Br_x$ is derived from a $CH_3Br$ source. A vertical profile for $Br_x$, obtained by averaging all of the 1976 and 1977 data, is given in Fig. 2. We have decided to ignore the anomalously high data point at 37 km. Indeed, for the last two altitudes, 32 and 37 km, a different air injection technique, used to collect the samples, might have led to spurious results. Alternatively,

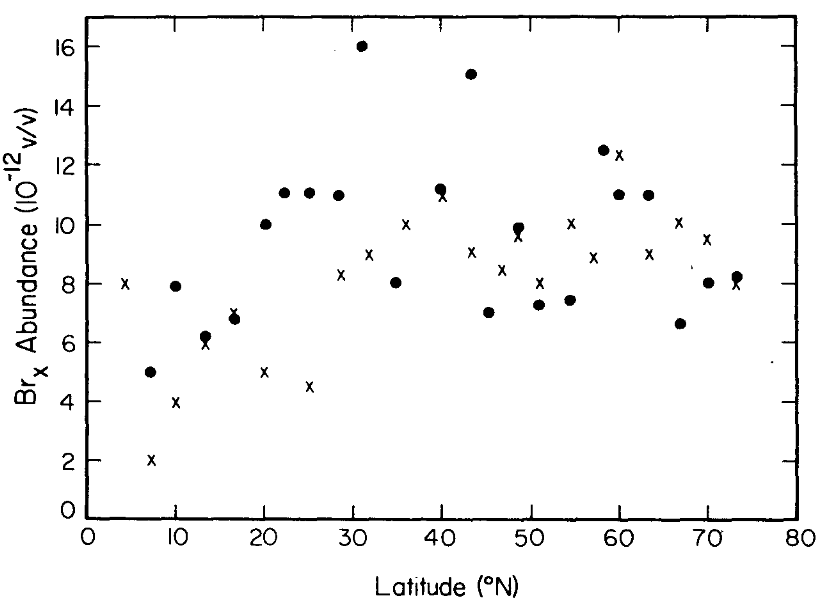


FIG. 1. Mixing ratio for total inorganic bromine $Br_x$ (=$Br + 2Br_2 + BrO + HBr + BrONO_2 + HOBr$) at 19 km from the equator to 70°N. The dots and crosses represent data taken in April 1976 and July 1977 by Lazrus *et al.* (1979).

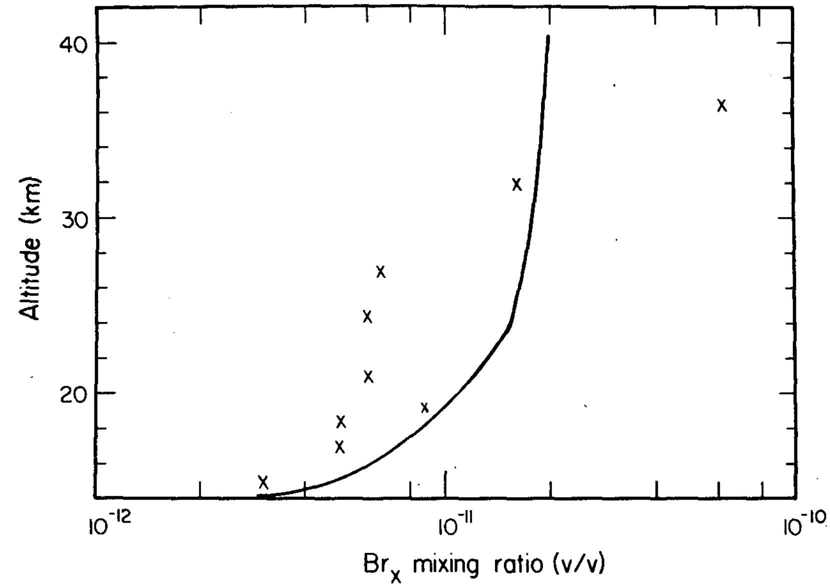


FIG. 2. Vertical distribution for $Br_x$ obtained by averaging all available data taken by Lazrus *et al.* (1979) in 1976 and 1977. The curve is obtained from model calculation by assuming that all $Br_x$ is derived from $CH_3Br$.

the collection efficiencies of the filters may have been influenced by the exceedingly reactive chemical environment in the middle and upper stratosphere. However, the anomalously high bromine values are reminiscent of Anderson *et al.*'s (1977) high chlorine values. These measurements may reflect our imperfect understanding of the sources of stratospheric halogens and the species partitioning amongst them.

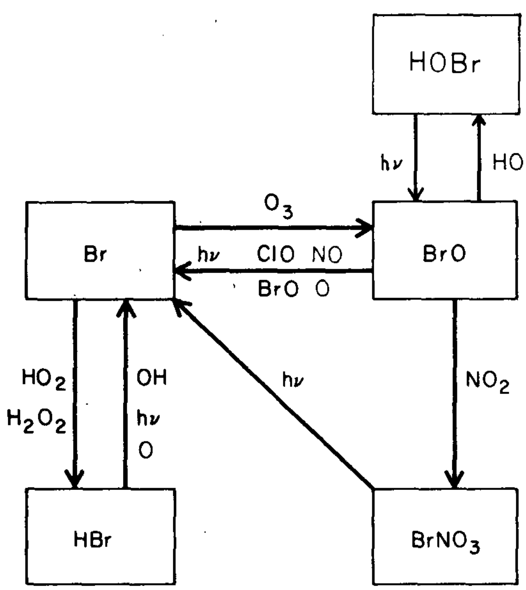


FIG. 3. Schematic diagram summarizing the major bromine species and their interactions.

The major bromine species in the stratosphere and important paths for cycling between species are schematically summarized in Fig. 3. Fig. 4 presents height profiles computed for BrO, $BrONO_2$, HBr, HOBr and Br in the present stratosphere with 20 pptv total bromine ($Br_x$), as prescribed by the profile shown in Fig. 2. The computations were carried out with a diurnally averaged one-dimensional photochemical model. Our model is based on a set of about 100 essential reactions recommended by NASA (1977), whose rate coefficients we adopt, except as otherwise stated in Tables 1a and 1b. We adopt the U.S. Standard Atmosphere model for 30°N, spring–fall season. Diurnally averaged photodissociation rates were obtained by integration over a 24 h cycle. Corrections to mean dissociation rates due to Rayleigh scattering and ground albedo for species that dissociate at wavelengths >200 nm are approximately made by modifying these quantities by factors taken from NASA (1977) and Wofsy (1978). The equations of continuity are solved from 0 to 80 km for all major $O_x$, $HO_x$, $NO_x$, $Cl_x$ and $Br_x$ species, and their precursors, allowing transport by eddy diffusion for long-lived species. We use Hunten's (1975) eddy diffusivity profile, with modifications recommended by NASA (1977). Altitude profiles of the major stratospheric free radicals computed by the photochemical model are given in Fig. 5. Unless otherwise stated, the number densities in Figs. 4 and 5 will be taken to be representative of the present atmosphere, containing 2.3 ppbv $Cl_x$, 19 ppbv $NO_x$, 6 ppmv $H_2O$ and 20 pptv $Br_x$ at 40 km. For these calculations, we

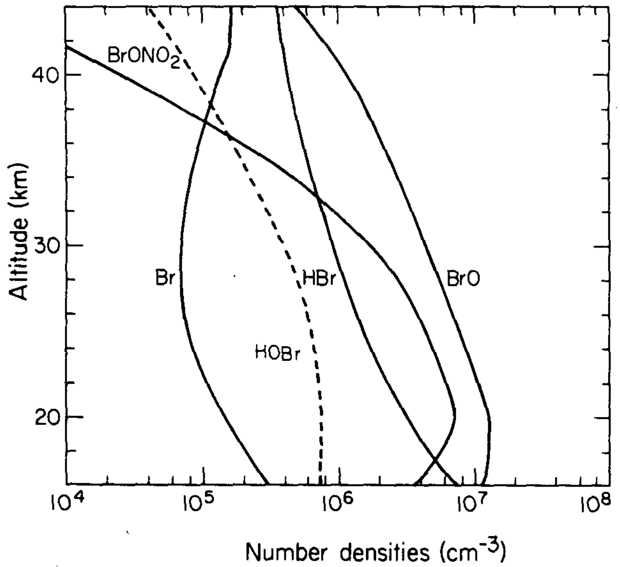


FIG. 4. Altitude profiles for major bromine species in the stratosphere, calculated using the reactions and rate coefficients of Table 1. Total $Br_x$ at 40 km equals 20 pptv.

have assumed a surface mixing ratio of 20 pptv for $CH_3Br$ (or total organic bromine), as suggested by the measurements. The mixing ratio of total inorganic bromine was 10 pptv at the ground (Wofsy *et al.*, 1975b). Heterogeneous removal of inorganic bromine, and other soluble trace constituents in the troposphere was modeled in the same way as Wofsy *et al.* (1975b). Our results, summarized in Fig. 4, show that BrO, an active form of bromine, is the major bromine species in the stratosphere, followed by $BrONO_2$, HBr, HOBr and Br. Here lies an important difference between the chemistry of bromine and chlorine. According to current models (see, e.g., Logan *et al.* 1978), the relatively inert forms of chlorine, HCl or $ClONO_2$ dominate over ClO throughout most of the stratosphere.

The presence of bromine at today's level is important in controlling the abundance of $O_3$ in the present atmosphere (with 2.3 ppbv of Cl). Fig. 6 shows a comparison of $O_3$ profiles computed with 0 and 20 pptv bromine. The difference in $O_3$ concentrations reaches 6% in the lower stratosphere, but effectively vanishes above 30 km. The column integrated ozone (from 0 to 80 km) for the two profiles in Fig. 6 differs by 2.4%. The result is somewhat surprising, that such a small amount of bromine can be so effective. Fig. 7 compares the rates of the bromine-related destruction of odd oxygen with other reactions, where "all others" is taken to be equal to $2k(O_3 + O) + 2k_{18}(HO_2 + O_3) + 2k_{17}(NO_2 + O) + 2k_{16}(ClO + O) + \frac{2}{3}J_{10}(ClONO_2) + k_{21}(HO_2 + ClO)$. The rate-determining reactions for cycles (I)–(V) are the reactions BrO + O (8), BrO + BrO (9), BrO + ClO (10a), BrO + $NO_2$ + M (11) and BrO + $HO_2$ (12), respectively. It is clear from Fig. 7 that the impact of bromine on ozone is mostly through cycle (III). Cycle (I) becomes active only in the upper stratosphere, where it competes rather unfavorably with "all others". On the other hand, cycle (III) peaks in the lower stratosphere, where it can act as a major additional sink for odd oxygen. Cycles (II), (IV) and (V) are insignificant compared with cycle (III) at current $Br_x$ and $NO_x$ levels. We now understand why the action of bromine on ozone is almost totally controlled by reaction (10a), and that factors of 3 uncertainty in

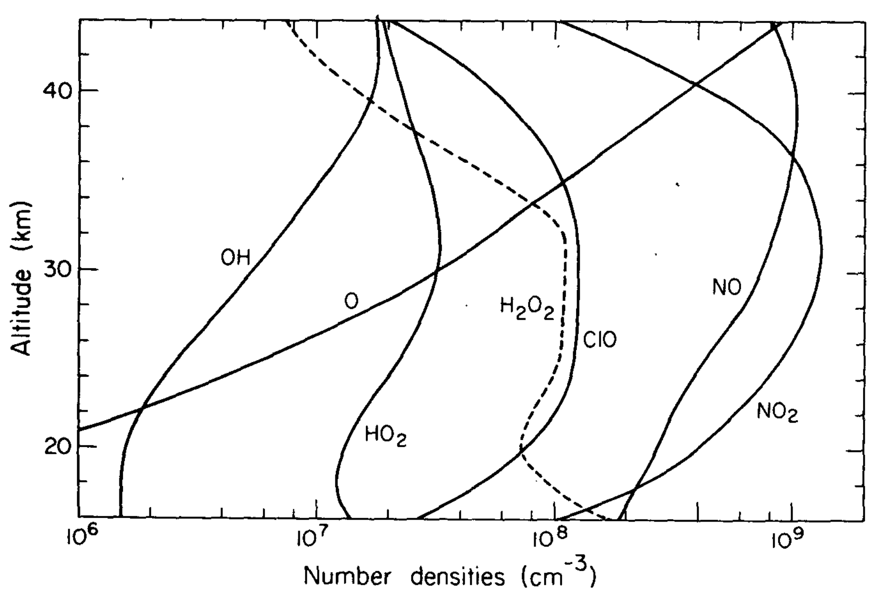


FIG. 5. Altitude profiles for important species in the stratosphere. The standard model contains 2.3 ppbv $Cl_x$, 19 ppbv $NO_x$, 6 ppmv $H_2O$ and 20 pptv $Br_x$ at 40 km.

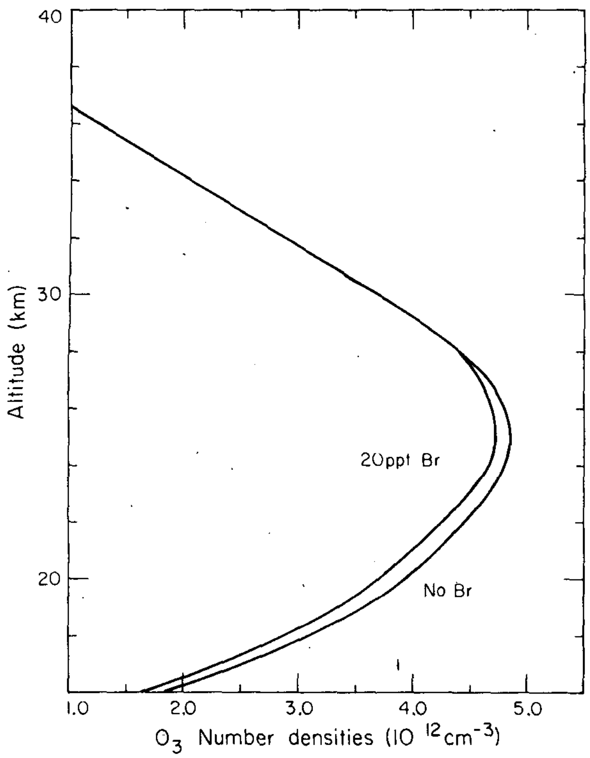


FIG. 6. Altitude profile for ozone computed with and without 20 pptv bromine.

reaction (8) are of no consequence. In all our computations, the production and loss of odd oxygen are calculated rigorously from the continuity equations. However, this procedure is equivalent to the use of catalytic cycles discussed here.

As discussed in the previous sections, bromine, when coupled with chlorine, can be an efficient catalyst for destroying ozone. This poses an obvious cause for concern over possible increases in atmospheric bromine as a result of future growth in the bromine industry. The importance of reaction (10a) in the lower stratosphere suggests that previous ozone depletion assessments (NAS, 1976; NASA, 1977) due to steady-state chlorofluoromethane release have been underestimated by not including the effects of bromine. We shall explicitly investigate two problems: 1) the depletion of ozone by bromine as the bromine concentration increases, while keeping the chlorine concentration fixed at its present level (2.3 ppbv); and 2) the depletion of ozone by chlorine due to steady-state chlorofluoromethane release at 1973 rates, while keeping the bromine concentration fixed at its present level (20 pptv).

In attacking the first problem, we must first estimate the source strength of bromine compounds in the present atmosphere. Table 2 lists a number of stable bromine compounds that can be derived from natural or anthropogenic sources, the global production rates required to maintain the steady-state abundances of the observed species, and the current world production rates for compounds that are widely used in industry. According to our estimates, the natural source of $CH_3Br$ should be around 35–70 × $10^9$ gm Br $year^{-1}$. The global industrial production rate of $CH_3Br$ in recent years has been about 14 × $10^9$ gm Br $year^{-1}$, which could account for 20–40% of the total atmospheric budget of $CH_3Br$, if all of it has been released to the atmosphere. However, there are increasingly larger demands for the agricultural use of methyl bromide,

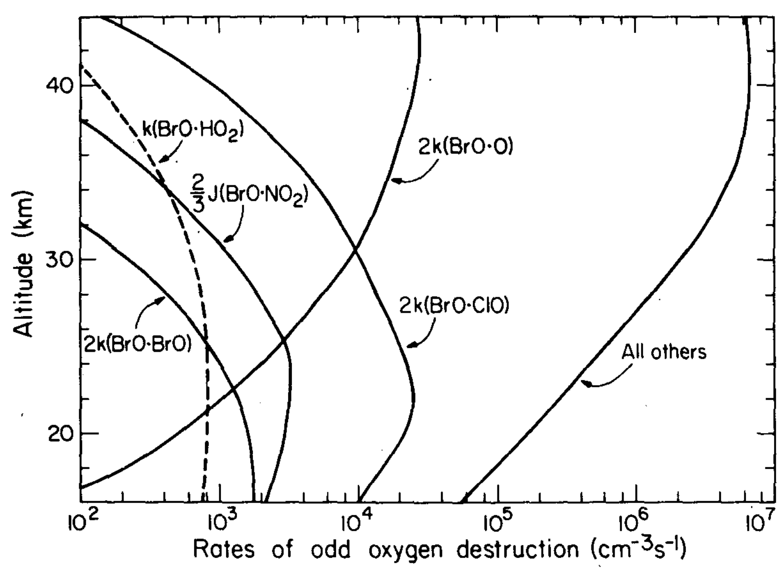


FIG. 7. Rates of the bromine-related destruction of odd oxygen. "All others" is the total odd oxygen destruction rate excluding that due to bromine (see text).

and its production has been rising since 1962 at the rate of 7% a year (Klingman, 1972–75; Foster, 1975–78). If this trend were to continue to the end of the century, the industrial source could exceed the natural source, and the bromine concentration in the atmosphere would greatly increase. Atmospheric bromine can also increase for another reason. The major sink for $CH_3Br$ and $C_2H_4Br_2$ in the troposphere is by reaction with OH. Wofsy (1976), Sze (1977) and Penner *et al.* (1977) have suggested that mean OH concentrations in the troposphere could decrease due to an increase in atmospheric CO. This could result in a longer lifetime for $CH_3Br$ and $C_2H_4Br_2$, and hence a higher concentration of these compounds, even if the sources remain constant. For similar reasons, the concentrations of chlorine containing compounds (e.g., $CH_3Cl$, $CHCl_3$, $CH_3CCl_3$) could also increase. There is at least one more potential future source of stratospheric bromine as pointed out by Spencer and Rowland (1978). The 1976 U.S. production of $CF_3Br$ was $0.75 \times 10^9$ gm Br.[2] The upper limit for the rate coefficient for reaction with OH, reported by Lebras and Combourieu (1978), implies a minimum tropospheric lifetime of 60 years. However, because the reaction is highly endothermic, it is more likely that $CF_3Br$ behaves like $CFCl_3$ and $CF_2Cl_2$ toward reaction with OH, and photolysis in the stratosphere is the major sink. We estimate a photolytic lifetime of 70 years for $CF_3Br$ based on the absorption cross-section data of Molina and Molina (1979). In this case, a constant industrial production rate as small as $1 \times 10^9$ gm Br year$^{-1}$ would result in a steady-state concentration of 5 pptv $CF_3Br$ in the lower atmosphere (assuming complete release to the atmosphere). Fig. 8 summarizes the results of the model calculations of ozone depletion as a function of bromine concentration in the atmosphere. In these calculations we take as "standard" a model atmosphere with 2.3 ppbv $Cl_x$ but no bromine. In the perturbation calculations, we assume that the vertical profile of $Br_x$ is the same as that due to a $CH_3Br$ source (see Fig. 2). The procedure should yield an exact answer if all stratospheric inorganic bromine is derived from $CH_3Br$, but must be considered as an approximation if other sources such as $CF_3Br$ and $CHBr_3$ become important. $\Delta O_3$ in the figure refers to the difference in column-integrated ozone abundance (from the ground to 80 km), and is nearly proportional to $Br_x$, at least to concentrations ~80 pptv.

Fig. 9 shows the results of model calculations of $O_3$ depletion due to steady-state chlorofluoromethane release at 1973 rates with and without including an amount of bromine equal to that in the present atmosphere. Curve $B_1$ is obtained by as-

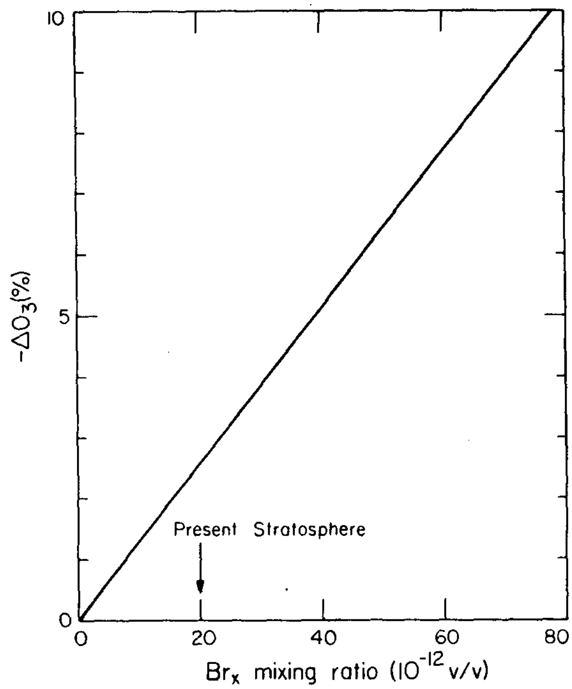


FIG. 8. Ozone depletion as a function of bromine concentration in the stratosphere. $\Delta O_3$ refers to the difference in column integrated ozone density (from 0 to 80 km). Calculations are summarized in Table 3.

suming that the present stratosphere contains 2.3 ppbv $Cl_x$, and that the perturbed atmosphere contains 8.2 ppbv $Cl_x$, reflecting a rise in chlorine concentration due to the release of chlorofluoromethanes. The concentrations of $CFCl_3$ and $CF_2Cl_2$ used to model the present and perturbed atmosphere are 0.1, 0.2, and 0.8, 2.3 ppbv, respectively. Following NAS (1976), we assume that yield of Cl atoms from $CFCl_3$ and $CF_2Cl_2$ photolysis are 2.5 and 2.0, respectively. Curve $B_3$ is obtained in the same way as curve $B_1$ with the additional assumption of the presence of 20 pptv bromine (as given by the profile in Fig. 2) in both the present and the perturbed atmosphere. To isolate the effect of cycles (V) and (VII), we also show curves $B_1$* and $B_2$*, which are obtained in the same manner as that for $B_1$ and $B_3$, but with the additional assumption that photolysis of $XONO_2$ (X = Br, Cl) proceeds by the path $XONO_2 \rightarrow XO + NO_2$ (or $O + XONO$) rather than the path $XONO_2 \rightarrow X + NO_3$. The effect on the vertically integrated ozone column abundance is summarized in Table 3. The difference between the present and previous assessments of the chlorofluoromethane impact on stratospheric ozone is about 11%. The difference would be greater (~17%) if cycles (IV) and (VII) were suppressed as in $B_1$* and $B_3$*. Our model predicts 0.2 ppbv $ClONO_2$ at 20 km, a value that should be compared with Murcray *et al.*'s (1978) upper limit of 0.3 ppbv (at 5% absorp-

[2] Based on data released to the EPA in 1977 by F. A. Bower of DuPont de Nemours & Co., Wilmington, DE.

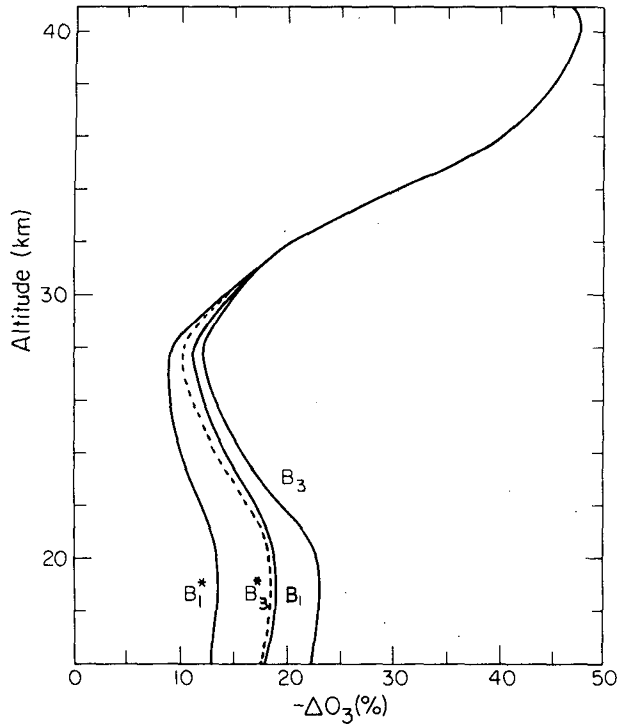


FIG. 9. Altitude profiles of ozone reduction due to steady-state chlorofluoromethane release at 1973 rates. $B_1$ is based on our standard model with no bromine; $B_3$ includes 20 pptv $Br_x$; $B_1$* and $B_3$* are the same as $B_1$ and $B_3$ except that photolysis for $XONO_2$ proceeds by the path $XONO_2 \rightarrow XO + NO_2$ or $O + XONO(X = Br, Cl)$. Details are referred to in Table 3.

tion level) at 20 km. As discussed earlier, the additional ozone depletion by bromine is primarily through the effect of cycle (III). The result for column-integration ozone depletion can be approximately expressed as

$$\frac{\Delta O_3[\text{cycle(III)}]}{O_3} \approx -\frac{1}{40}\left(\frac{Br_x}{(Br_x)_0}\right)\left(\frac{Cl_x}{(Cl_x)_0}\right)^{1/3},$$

where $(Br_x)_0 = 20$ pptv, $(Cl_x)_0 = 2.3$ ppbv, $Br_x \leq 100$ pptv and 2 ppbv $\leq Cl_x \leq 10$ ppbv. The exponent 1/3 in $Cl_x$ acts as a damping factor and is due to a "self-healing" effect caused by the destruction of $O_3$ at high altitudes. More photons are then allowed to penetrate deeper into the atmosphere where they can photolyze $O_2$. With bromine, however, most of the $O_3$ perturbation takes place in the lower stratosphere below the level of maximum concentration for $O_3$, and the corresponding radiative feedback is absent. Our results for $\Delta O_3$ fall between curves A and B, in Fig. 2 of Wofsy *et al.* (1975b). It is not meaningful to seek a more detailed comparison between Wofsy *et al.*'s calculations and ours since the major catalytic cycles and the number densities of important chemical species in the two models are different. Some photochemical models (see, e.g., Derwent and Eggleton, 1978) predict lower concentrations of ClO in the lower stratosphere, for reasons to be discussed in the next paragraph, and the bromine effect is accordingly smaller. Our calculations are based on diurnally averaged values for all stratospheric species. A fully time-dependent calculation will (i) increase the daytime ClO concentration due to $J_{10}$; (ii) increase the daytime BrO concentration due to $J_1$; and (iii) decrease the daytime BrO concentration due to $J_2$ and NO. At low values for $J_2(\leq 3 \times 10^{-3}\ s^{-1})$, (ii) is much larger than (iii), and our calculations have underestimated the effect of bromine. A comparison between time-dependent and diurnally averaged calculations has been performed by Sze (1979, private communication) using a similar photochemical model with $J_2 = 1 \times 10^{-2}\ s^{-1}$. Sze's results are close to ours. However, his time-dependent calculations predict a 30% larger $\Delta O_3$ than is obtained with the diurnally averaged model.

A number of uncertainties in the current modeling effort of stratospheric bromine can be readily identified. The major bromine-related catalytic cycle is cycle (III), whose effect on $O_3$ is, to first order, given by

$$-\delta O_3 \propto 2k_{10a}[ClO][BrO].$$

In the lower stratosphere, we can derive approximate expressions for ClO and BrO:

TABLE 3. Column-integrated (from 0 to 80 km) ozone abundance calculated by our photochemical model for various concentrations of $Cl_x$ and $Br_x$ in steady state. The units for ozone, $Cl_x$ and $Br_x$ abundances are cm-atm (1 cm-atm = 2.6 $\times 10^{19}$ molecules $cm^{-2}$), ppbv and pptv, respectively. For cases marked by an asterisk we assume that photolysis of $XONO_2$ proceeds by the path $XONO_2 \rightarrow XO + NO_2$ (or $O + XONO$), where X = Br or Cl. For all other cases, photolysis of $XONO_2$ proceeds by the path given in Table 1. Runs $C_1$, $C_2$, $D_1$ and $D_2$ show the sensitivity of the results for $A_3$ to the uncertainties in the rate coefficients for reactions $2(Br + HO_2)$ and $J_2(BrO + h\nu)$. For runs $C_1$ and $C_2$, $k_2$ was set equal to $4 \times 10^{-11}$ and $5 \times 10^{-12}\ cm^3\ s^{-1}$, respectively, in runs $D_1$ and $D_2$, $J_2$ was set equal to $3 \times 10^{-2}$ and $3 \times 10^{-3}\ s^{-1}$.

| | $Cl_x$(ppbv) | | |
|---|---|---|---|
| $Br_x$(pptv) | 2.3 | 8.2 | $\Delta O_3/O_3 = \frac{B}{A} - 1$ |
| 0 | $A_1$ 0.327 | $B_1$ 0.268 | −18.0% |
| 10 | $A_2$ 0.323 | $B_2$ 0.262 | −18.9% |
| 20 | $A_3$ 0.319 | $B_3$ 0.256 | −19.7% |
| 30 | $A_4$ 0.315 | $B_4$ 0.251 | −20.6% |
| 80 | $A_5$ 0.294 | $B_5$ — | — |
| 0 | $A_1$* 0.333 | $B_1$* 0.283 | −15.0% |
| 20 | $A_3$* 0.326 | $B_3$* 0.269 | −17.5% |
| 20 | $C_1$ 0.321 | | |
| 20 | $C_2$ 0.318 | | |
| 20 | $D_1$ 0.321 | | |
| 20 | $D_2$ 0.319 | | |

$$\frac{[\mathrm{Cl}]}{[\mathrm{Cl}_x]} \approx \left\{1 + \frac{k_{25}k_{31}[\mathrm{CH_4}][\mathrm{NO}]}{k_{32}k_{15}[\mathrm{OH}][\mathrm{O_3}]} + \frac{k_{19}[\mathrm{M}][\mathrm{NO_2}]}{J_{10}}\right\}^{-1},$$

$$\frac{[\mathrm{Br}]}{[\mathrm{Br}_x]} \approx \left\{1 + \frac{k_2[\mathrm{HO_2}](J_2 + k_7[\mathrm{NO}])}{k_1k_5[\mathrm{OH}][\mathrm{O_3}]} + \frac{k_{11}[\mathrm{M}][\mathrm{NO_2}]}{J_1}\right\}^{-1}.$$

The quantities most critical for a better understanding of stratospheric bromine are summarized and critiqued in Table 4. For simplicity, we choose to evaluate all the relevant quantities at 20 km. We may note that ClO in the lower stratosphere is a minor chlorine species, whose concentration is controlled by NO, $NO_2$, $k_{25}$ and $CH_4$. A comparison between predicted and measured ClO concentrations below 25 km shows considerable disagreement (Anderson *et al.*, 1977), with the measurements suggesting lower ClO concentrations, especially in winter. If the missing ClO has been converted into HCl, this would result in a net decrease in the catalytic destruction of $O_3$ in the lower stratosphere. However, if the missing ClO has been converted into $ClONO_2$ and if the photolysis products are Cl + $NO_3$ [Murcray *et al.*'s, (1978) upper limit measurement of $ClONO_2$ is for March], then cycle (VII) would operate in favor of cycle (III), and lead to a net destruction of $O_3$. The major uncertainty in the bromine chemistry is the absolute concentration of $Br_x$. The way in which the uncertainties in Table 4 affect $\delta O_3$ is, in most cases, explicitly given by the approximate expressions we derived earlier. We do, however, include in Table 3 the results of four runs ($C_1$, $C_2$, $D_1$, $D_2$) on the sensitivity of $\delta O_3$ to a range of values for $k_2$ and $J_2$. The results suggest that $\delta O_3$ does not vary by more than 50% over the considerable uncertainty range for $k_2$ and $J_2$, except in the unlikely event that $k_2$, $J_2$ and $k_5$ all happen to take on extreme values which would lower the [BrO] to [$Br_x$] ratio. We have also examined the sensitivity of the results to the choice of eddy diffusivity profile. A factor of 1.5 increase or decrease in values of eddy diffusivities leads to a 20% decrease and a 20% increase in $\delta O_3$, respectively. In addition to the uncertainties associated with the photochemistry in our model, there is the question of whether the one-dimensional model approach is really valid for modeling the lower stratosphere.

It is well known that dynamical processes play a major role in determining the distributions of ozone and other trace gases in the lower stratosphere. The one-dimensional model considers vertical transport only, whereas the motion field is more nearly horizontal. Quasi-horizontal motions transport trace gases poleward, where they will meet different conditions of temperature and the availability of solar ultraviolet radiation. These variations will play an important role in determining the species partitioning between the total inorganic chlorine and bromine reservoirs. The relative importance of either HCl or $ClNO_3$ (as chlorine reservoirs) on the destruction of ozone at high latitudes has already been mentioned. A detailed treatment of stratospheric-tropospheric exchange processes is also required, in order to accurately determine the lifetime, in the lower stratosphere, of substances which may deplete ozone. Indeed, the study of compositional changes in the lower stratosphere on ozone may require the use of a multi-dimensional dynamical model.

TABLE 4. The major uncertainties in the modeling of the coupled photochemistry of bromine in the lower atmosphere.

| Quantity | Magnitude at 20 km | Uncertainty |
|---|---|---|
| $Cl_x$ | 0.99 ppbv | factor of 1.5 |
| $Br_x$ | 11 pptv | factor of 2 |
| $k_{10a}$ | $6.7 \times 10^{-12}$ cm$^3$ s$^{-1}$ | $2.5 \times 10^{-12} - 1.3 \times 10^{-11}$ cm$^3$ s$^{-1}$ |
| $k_{25}$ | $1.6 \times 10^{-14}$ cm$^3$ s$^{-1}$ | $1.3 - 2.1 \times 10^{-14}$ cm$^3$ s$^{-1}$ |
| NO | $2.7 \times 10^8$ cm$^{-3}$ | factor of 2 |
| ClO | $7.8 \times 10^7$ cm$^{-3}$ | factor of 2 (see text) |
| $J_2$ | $1 \times 10^{-2}$ s$^{-1}$ | $3 \times 10^{-2} - 3 \times 10^{-3}$ s$^{-1}$ |
| $k_2$ | $2.0 \times 10^{-11}$ cm$^3$ s$^{-1}$ | $4 \times 10^{-11} - 5 \times 10^{-12}$ cm$^3$ s$^{-1}$ |
| $k_5$ | $8.5 \times 10^{-12}$ cm$^3$ s$^{-1}$ | factor of 1.5 |
| BrO | $1.2 \times 10^7$ cm$^{-3}$ | factor of 2 |

## 4. Conclusions

In the lower stratosphere (16–26 km) ozone can be efficiently removed by a mixed bromine-chlorine catalytic cycle [cycle (III)], with additional contributions from cycle (IV) and cycle (VII). All three cycles involve a synergistic coupling between radical species from different families. We have investigated the effect of bromine in the present atmosphere, and in an atmosphere perturbed by large concentrations of halogens derived from anthropogenic sources. In both cases, the results (summarized in Table 3) suggest that bromine is important for controlling stratospheric ozone at a few percent level, and should be included in photochemical models. The major uncertainties in the modeling of bromine chemistry are in the concentrations of ClO and $Br_x$ in the lower stratosphere and the rate coefficients for the key reactions $k_{10a}$, $k_2$ and $J_2$ (see Table 4). These uncertainties can be removed by suitable experimental work in the future. This work raises the possibility of large ozone depletions (20–30%) in the lower stratosphere, associated with the release of chlorofluoromethanes.

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